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## Details

### 1. Title of the invention

Molded material for optical purposes

### 2. Scope of claims

1. Molded material for optical purposes, which is a mixture of polyphenylene ether with weight average molecular weight in the range of 40000 ~ 70000 (in terms of polystyrene) and polystyrene resin where,

① The ratio of molecular weights is

$$2 \leq \text{PsMw} / \text{PPMw} \leq 5 \dots (1)$$

(Where PPMw means weight average molecular weight of polypropylene ether converted into that of polystyrene and PsMw means weight average molecular weight of polystyrene)

② The ratio of composition is

$$80 / 20 \leq \text{Ps} / \text{PP} \leq 55 / 45 \dots (2)$$

(Where, PP means composition of polyphenylene ether by weight).

2. Molded material for optical purposes mentioned in claim 1 above, in which the polyphenylene ether is poly (2,6-dimethyl-1,4-phenylene) ether.

3. Molded material for optical purposes mentioned in claim 1 above, in which the polyphenylene ether is a copolymer of 2,6-dimethyl phenol and 2,3,6-trimethylphenol.

4. Molded material for optical purposes mentioned in claim 1 above, in which the polystyrene resin is polystyrene.

5. Molded material for optical purposes mentioned in claims 1,2 and 3 above, in which the difference in absolute values of double refraction occurring for  $\pm 30^\circ$  angle of vertical and inclined incident light beam is within 50 nm at thickness of 1.2 mm.

6. Molded material for optical purposes mentioned in claims 1,2 and 3 above, in which the permeability of optical beam of light at 1.2 mm thickness and 500 ~ 1600 nm is at least 85 %.

### **3. Detailed description of the invention**

This invention is concerned with a new molded material for optical purposes made from a resin composition composed of a mixture of polyphenylene ether and polystyrene, having a specific molecular weight ratio and weight ratio. As it has especially low optical distortion and excellent optical properties, it is suitable for optical lenses.

## **Conventional techniques and problems**

Conventionally, acrylic resin is known as transparent molded product for optical use because of its good fluidity, low double refraction (Patent No. JP56-131654). However, thermal resistance of acrylic resin is as low as 70°C and its impact strength is also low and it easily warps in moisture. For removing the above defects, use of polycarbonate with viscosity average molecular weight of 15000 ~ 18000 by molding it into disk or lenses, has been proposed (Patent No. JP58-180553). However, in that case, double refraction (which is an important property) is high.

Further, one of the important issues in case of practical application of optical material and mainly optical disk material is reducing the noise level of the substrate itself. It has been made clear that this problem has originated from the double refraction including the light incident obliquely (for example, 'Kougaku' (Optics) vol. 15, No. 5 (October 1986) p 441 ~ 421. Optical Memory Symposium 1986 Abstracts p 33~38).

Reduction of double refraction of vertically incident light may not be necessarily correlated with that of inclined light and especially in case of polycarbonate, this difference is more pronounced. Reduction of double refraction in the obtuse angle region is thus important.

As far as vertically incident light is concerned, a mixture of polycarbonate and polystyrene has been proposed as a polymer having anisotropy for reducing double refraction (for example, Patents JP 61-19630, JP19656, JP62-20524 and JP61-10817). This system is non-compatible and therefore in a simple mixture, there is a tendency to form a coarse dispersion.

As a result, if the micro dispersed phase becomes larger than  $0.5\ \mu\text{m}$  (say  $3\ \mu\text{m}$ ), there occurs difference in the double refraction in the individual optical paths and this un-evenness causes noise in the micro size region even if the double refraction becomes 0 and the surface of dispersed particles becomes the source of scattering. This optical un-evenness causes noise.

On the other hand, from the point of molecular orientation analysis, the method of mixing two mutually anisotropic polymers in the form of solution and observing the orientation of molecules from the result of mutual reduction of double refraction, is well known. (for example, Polymer, 1981, vol. 22, Dec. 1616; Polymer, 1982, vol. 22 May, 706; US 4373 065). Thus in the conventional method, poly (phenylene ether) and polystyrene (which are mutually anisotropic) are mixed in solution and a film is generated by removing the solvent. Then variation of the double refraction of this film in elongated condition is observed. From the values of elongation ratio of the polymer and variation in double refraction, optical elasticity coefficient is found out. Elongation of the film produces double refraction because of expansion-orientation of the resin. Molding gives rise to double refraction due to fixing of the fluid resin, and the fact that their difference is a major issue, can be easily understood. Thus the problem of double refraction occurring mainly in injection molding (double refraction of vertically incident light and double refraction of obliquely incident light) is not somehow solved and practical application was not possible.

Now, one of the important criteria in case of optical material is that the material must be transparent. Usually, it is said that the lowering of total optical transparency results from the basic chemical structure of the structural unit or oxidative polymerization. This was a major

obstacle for using polyphenylene ether as optical material. The fact is that there is no available example of using a resin composition containing polyphenylene ether.

### **Procedure for solving the problems**

The present inventors conducted intensive research work on molded material that shows lesser optical distortion especially at obtuse angle and possesses optical evenness and transparency. As a result, it was observed that a transparent molded material for optical purposes can be obtained from a resin composition which is a mixture of polyphenylene ether and polystyrene resin, having the average molecular weight ratio and weight composition in a specific range and this led to the present invention.

Thus this invention presents a molded material for optical purposes, which is a mixture of polyphenylene ether with weight average molecular weight in the range of 40000 ~ 70000 (in terms of polystyrene) and polystyrene resin where,

① The ratio of molecular weights is

$$2 \leq \text{PsMw} / \text{PPMw} \leq 5 \dots (1)$$

(Where PPMw means weight average molecular weight of polypropylene ether converted into that of polystyrene and PsMw means weight average molecular weight of polystyrene)

② The ratio of composition is

$$80 / 20 \leq \text{Ps/PP} \leq 55 / 45 \dots (2)$$

(Where, PP means composition of polyphenylene ether by weight and Ps is the composition of polystyrene by weight). In practice, the polyphenylene ether is poly (2,6-dimethyl-1,4-phenylene) ether and the polystyrene resin is polystyrene. Further, the absolute value of double refraction at vertically incident light beam and  $\pm 30^\circ$  inclination is up to 50 nm at 1.2 mm thickness.

The polyphenylene used in this invention is the one having its weight average molecular weight (in terms of polystyrene) (=PPMw; a value measured by GPC method on the basis of polystyrene mentioned in Note 1 mentioned later) in the range of 40,000 ~ 70,000 and having intrinsic viscosity of 0.040 ~ 0.55 (Note 2 mentioned later). Further, in relation with the other component that is polystyrene resin, the ratio of PPMw and weight average molecular weight of polystyrene (PsMw) is in the range mentioned in the equation (1) above.

In the molded product of this invention for optical purposes, the respective components of polyphenylene ether and polystyrene resin are selected in such a way that the ratio of weights of polyphenylene ether (= PP) and weight of polystyrene resin (= Ps) is in the range shown by equation (2)' namely

$$75 / 25 \leq Ps / PP \leq 65 / 35 \dots (2)'$$

Desirable results are obtained in this invention when the weight average molecular weight of polyphenylene ether in terms of polystyrene satisfies all the equations namely equation (1) and (2) [and (2)'] and these things are interdependent. When these are combined in optimum proportion, the double refraction in both vertically incident light and inclined light (ref. Note

3 mentioned later) is within  $\pm 10$  nm and even if the injection conditions (especially injection temperature) vary during molding process in the range of  $280 \sim 320^{\circ}\text{C}$ , the absolute value of double refraction varies at the most by 30 nm. **Thus independent decision about these things is purely secondary and this can be explained as follows.** If the weight average molecular weight of polyphenylene ether (= PPMw) in terms of polystyrene is less than 40,000, the mechanical properties and thermal resistance of the molded product are affected and, if it exceeds 70,000, it poses difficulty for molding. Equations (2) and [(2)'] are mainly concerned with the distortion occurring in case of obtuse angle and if this range is exceeded, the difference in double refraction occurring in  $\pm 30^{\circ}\text{C}$  in vertical and inclined incident beam cannot be reduced. Equation (1) is mainly related to the absolute value of double refraction and if the above range is exceeded, the dependence of double refraction on molding temperature increases and it is not desirable.

For the molded product of this invention, polystyrene resin is mixed uniformly in the ratio of formula (2) and [(2)'] and then by using an optical beam in the wavelength range of  $500 \sim 1600$  nm and desirably  $600 \sim 1600$  nm, it is possible to maintain transparency of at least 85%. Thus by specifying the wavelength region, it has become possible to use it appropriately for optical products like optical disk or lenses.

In the wavelength region in the above-mentioned range, that is at a wavelength below 500 nm, the optical transparency reduces and it is not desirable.



Molding temperature for the material for this invention is 200 ~ 360°C and the desirable value is 240 ~ 340°C. At a temperature lower than the one mentioned above, the fluidity is not good and at higher temperature coloring of the resin or so called "burning" may take place and it is not desirable. The polyphenylene ethers that are useful for the purpose of this invention are homopolymer (for example the one mentioned in US patent No. 3,306,877) obtained from 2,6-dialkylphenol and copolymer of 2,6-dialkylphenol and 2,3,6-trialkylphenol (USP 4,011,200). Usually it is produced by oxidative coupling of 2,6-dialkylphenol (for example 2,6-dimethylphenol) alone, or its mixture with 2,3,6-trialkylphenol (for example 2,3,6-trimethylphenol). For producing the copolymer suitable for this invention, the proportion of 2,3,6-trialkylphenol is about 2 ~ 50 weight % as against total polyphenylene ether. However, desirable copolymer can be obtained from about 2 ~ 20 weight % (desirably 2 ~ 10 weight %) of 2,3,6-trialkylphenol and 98 ~ 80 weight % (desirably 98 ~ 80 weight %) of 2,6-dialkylphenol as against 2,3,6-trialkylphenol. Oxidative coupling is a well-known method for homopolymerization or co-polymerizing these. This type of polymer is obtained commercially.

The above homopolymer of alkylphenol and copolymer, especially homopolymer prepared from 2,6-dimethylphenol and copolymer prepared from 2,6-dimethylphenol and 2,3,6-trimethylphenol easily form a single composition because of their compatibility with polystyrene. Examples of polystyrene that can be used in this invention are homopolymers like poly- $\alpha$ -methylstyrene and poly-p-methylstyrene and styrene-containing copolymers like styrene-maleic anhydride copolymer, styrene-maleimide copolymer, styrene-acrylonitrile copolymer and styrene-acrylonitrile-methylstyrene three dimensional copolymer. However, especially suitable one is homopolystyrene.

Well-known methods like fused mixing by using extrusion machine, kneader or Banbury mixer can be used for uniform mixing of polyphenylene ether and styrene based resin. Alternatively, they are dissolved in known solvents like chloroform or toluene and the solutions are mixed and the solvent is removed.

In case of the mixture of polyphenylene ether resin and styrene resin thus obtained in this way, it is better to control the coloration due to decomposition of the resin and reduction of transparency by the addition of 0.01 ~ 2 weight % phosphite ester as against the composition. In such a case, examples of phosphite ester are tributyl phosphite, tris (2-ethylhexyl) phosphite, tridodecyl phosphite, triphenyl phosphite, tricresyl phosphite, 2-ethylhexyl phenylphosphite, tricyclohexyl phosphite, and distearyl penta erythrityl diphosphite.

The addition the above phosphite esters is done by dry blending, fused mixing while palletizing, by means of extrusion machine or making master pellets having higher concentration of phosphite ester and dry blending them with the pellets.

### **Application examples**

This invention is further explained below by giving application examples. Weight average molecular weight (in terms of styrene), viscosity, double refraction, light beam permeability (transparency), and water absorption were measured by the following methods.

Note 1: Weight average molecular weight in terms of polystyrene: It is the weight average molecular weight obtained by taking polystyrene as the standard (reference) by G.P.C.

Note 2: Viscosity: Measured by the following method.

- (1) Sample solution: Chloroform solution of concentration 0.2 g/dl
- (2) Viscometer: Improved capillary type Ubbelohde viscometer with 76.7 seconds flow time for chloroform only.
- (3) Measurement temperature:  $30^{\circ}\text{C} \pm 0.01^{\circ}\text{C}$

Note 3: Double refraction: Measured by the following method.

(1) Sample and apparatus

Sample for measurement: Injection molded disk of thickness 1.2 mm, diameter 130 mm

Wavelength of measurement: 632.8 nm

Measuring instrument: Mizoshiri Kogaku Industries, Auto ellipsometer

(2) Double refraction for vertical and inclined radiation

① Double refraction for vertical radiation ( $\text{Re}^0$ ):

Angle of incidence with respect to the sample

Represents double refraction for Horizontal angle  $H = 0^{\circ}$ , Vertical angle  $V = 0^{\circ}$ .

Horizontal angle means angle in the radial direction of disk and vertical angle means angle in the direction vertical to the radial direction of disk.

② Double refraction in inclined direction ( $\text{Re}^{\max 30}$ ):

Angle of incidence with respect to the sample surface

Represents maximum of the absolute value of the difference of double refractions at Horizontal angle  $H = \pm 30^\circ$ , Vertical angle  $V = \pm 30^\circ$  and double refraction for vertical radiation ( $Re^\circ$ ).

Note 4: Optical beam permeability

- (1)Sample: Injection molded product of thickness 1.2 mm
- (2)Measuring instrument: Automatic recording intensity meter
- (3)Wavelength of measurement: 830 nm unless otherwise stated

Note 5: Haze

- (1)Sample: Molded product of thickness 1.2 mm
- (2)Measuring instrument: Nippon Denshoku Industries Haze meter

Model 1001DP

Note 6: Moisture absorbance: Equilibrium moisture absorbance in distilled water at  $23^\circ\text{C}$  was measured on the basis of ASTM D-570.

Following short forms are used in the examples.

PEC = Copolymer of 2,6-dimethylphenol (95%) and 2,3,6-trimethylphenol (5%), basically produced according to USP 4,011,200.

H-PPE = Homopolymer of 2,6-dimethyl phenol, essentially produced according to USP 4,011,200.

Ps = Polystyrene

Ps1 = Manufactured by Shin Nippon Tetsu Kagaku Co. Trade name: EstiraneG32.

Ps2 = Produced according to the usual method.

Ps3 = Manufactured by Mitsubishi Monsanto Kasei Co. Trade name: Dialex HH102

Ps4 = Manufactured by Shin Nippon Tetsu Kagaku Co. Trade name: EstiraneG20.

Ps5 = Produced by the usual method.

Pc = Manufactured by Mitsubishi Gas Chemicals Co. Trade name:Yupiron H-4000,

viscosity

average molecular weight 16000.

#### **Application examples 1 ~ 10**

In a biaxial extruding machine, at 240 ~ 300°C, the components PEC 1 ~ 3, H-PPE 1 ~ 3 and Ps 1 ~ 3 were homogenized and injection molded.

Cylinder temperature during injection molding, double refraction, optical beam permeability, haze and moisture absorption are presented in Table 1.

#### **Comparison examples 1 ~ 4**

In a biaxial extruding machine, at 240 ~ 300°C, the components Pc alone and components PEC 3, H-PPE 4 and Ps 4.5 were homogenized and injection molded.

Cylinder temperature during injection molding, double refraction, optical beam permeability, haze and moisture absorption are presented in Table 2.

(Title of Table 1): **Application examples**

Only Japanese matter in the Tables is translated.

**Table 1 Column 1**

Cylinder temperature °C

Double refraction nm

Optical permeability %

Haze %

Moisture absorption %

**Table 2 Column 1**

Cylinder temperature °C

Double refraction nm

Optical permeability %

Haze %

Moisture absorption %

**Table 2** application example 2, row 9: -200 and above, not possible

**Table 2** application example 3, row 8: Injection molded product could not be produced

**Table 2** application example 4, row 9: -200 and above, not possible

**Table 2** last column heading: Remarks

**Table 2** last column, row 8: 1): cracked during molding

**Table 2** last column, row 10: 2): Measured at wavelength 450 nm

### **Effect of this invention**

As it is clear from the detailed description of this invention, application examples and comparison examples, the resin composition for optical purposes of this invention consisting polyphenylene ether as the main component has greatly reduced the difference between double refraction for vertical and inclined light beam and made it possible to set their absolute values also within  $\pm 10$  nm and the composition is optically uniform.

In addition to this, the noise originating from optical non-uniformity as well as that originating from double refraction has been very much reduced.

Further, since the injection-molded product has very low temperature dependence, it can be used for optical disks, and lenses for optical purposes.